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On the L_I X-ray absorption spectrum of metallic and vitreous selenium and of selenium dioxide

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With 2 figures in the text

ABSTRACT

The Se L_I absorption edge of metallic and vitreous selenium and of selenium dioxide is recorded and measured. Close agreement in the shapes of the edges of the vitreous form and the oxide is found while the edge of metallic selenium is somewhat different. The energy shift between the two former edges is 4.2 eV.

Introduction

The L_I, L_{II} and L_{III} absorption edges of selenium have been photographically recorded by Sandström (1). The K absorption edge has also been photographically registered by Hulubei and Cauchois (2). Recently Givens, Koester and Goffe (3) have recorded the $M_{IV,V}$ absorption edge of selenium, distinguishing between selenium in the metallic and vitreous states. The X-ray intensity was detected by photographic means, but the absolute absorption coefficient and its variation was determined. Valence band studies of selenium are of special interest as this element appears both as a semi-conductor (metallic state) and as an insulator (vitreous state). To investigate these properties the present work was undertaken.

The spectrograph and other devices used in this investigation are the same as in previous reports (4). The voltage applied to the X-ray tube was kept below twice the ionization potential of the Se L_I energy level to avoid order correction. The continuous spectrum from a tungsten target gave the X-ray intensity. The filling of the Geiger-Müller counter consisted of 3 % butane and 97 % argon at a total pressure of 400 mm Hg.

Preparation of the foils

For all the foils used the substance was evaporated on a polystyrene sheet (surface density 200 mg/cm^2) in a vacuum furnace at an air pressure below $5 \cdot 10^{-6}$ mm Hg. The backing was made large enough to cover two equally large windows in a metal frame. First a very thin film of the selenium sample (some hundreds of Ångströms) was evaporated onto both windows. The furnace was opened for short time, a glass plate was mounted in front of one of the windows while the other was left uncovered, and with a bigger sample in the cradle the evaporation was continued. The deposit on the glass plate was weighed and the surface density calculated, this being the same as the surface density of the extra selenium deposit on the uncovered window. During the recording the incident intensity was measured through the window which had been covered by the glass plate and the transmitted intensity through the other window. The absorption coefficient could be calculated by means of these intensities for the known surface density of the absorbing "difference" layer.

By measuring the incident and transmitted intensities as described interface disturbances between substance and backing are automatically neutralized. That such disturbances might cause distortion in the absorption curve in the ultraviolet region has been shown by Tomboulian (5).

As the amount of selenium deposited on the glass plate was too small to be weighed with good accuracy, a selenium foil of greater "difference" thickness (about 3–4 times the optimum thickness) was made in the same way as earlier mentioned. The quotient between the absorption coefficients of the thick foil and the thin one was evaluated for three different wavelengths in the neighbourhood of the absorption edge and was found constant. By division of the surface density of the thick foil by this constant a better value for the surface density of the thin foil was obtained, the relative error being $\pm 2\,\%$.

The absorption curves in Fig. 1 have been registered with foils of the following surface densities: metallic selenium 0.163 mg/cm^2, vitreous selenium 0.260 mg/cm^2 and selenium dioxide 0.413 mg/cm^2. The samples consisted of spectroscopically standardized material from Johnson, Matthey & Co.

Heating of vitreous selenium at a certain temperature converts it into metallic form. As the change of modification is accompanied by a contraction of 15 %, a deposit of vitreous selenium on polystyrene is transformed into metallic grains and islands. The inhomogeneity of such a foil makes it useless as an absorber. A method consisting in coating the substrate with a thin tellurium layer before the vitreous selenium is superimposed has been reported by P. Givens (6). Tellurium adheres to polystyrene, and as it has the same crystal form as selenium metal the tellurium film controls the formation of a smooth homogeneous selenium layer when it is heated.

A layer of about 40–50 Ångströms of tellurium was evaporated onto a polystyrene backing and after that vitreous selenium was evaporated by the procedure earlier described. Heat treatment at 75° C for 24 hours in an oven gave metallic selenium foils without scratches, as could be seen in a microscope. By reflected light the metallic modification shows a grey lustrous colour but in transmitted light it is red like the vitreous form. To test that there was no intermingling between the two modifications, a metallic and a vitreous foil were crushed and soaked in carbon disulphide in different test tubes for some days. The former did not change while the latter was completely dissolved and coloured the solvent.

Measurements

As can be seen from Fig. 1 the change in absorption at the edge is less than 15 % of the background absorption and therefore a comparatively long time is necessary for every determination of the absorption coefficient. The points of the curves are mean values of two runs and in each run the mean was taken of three

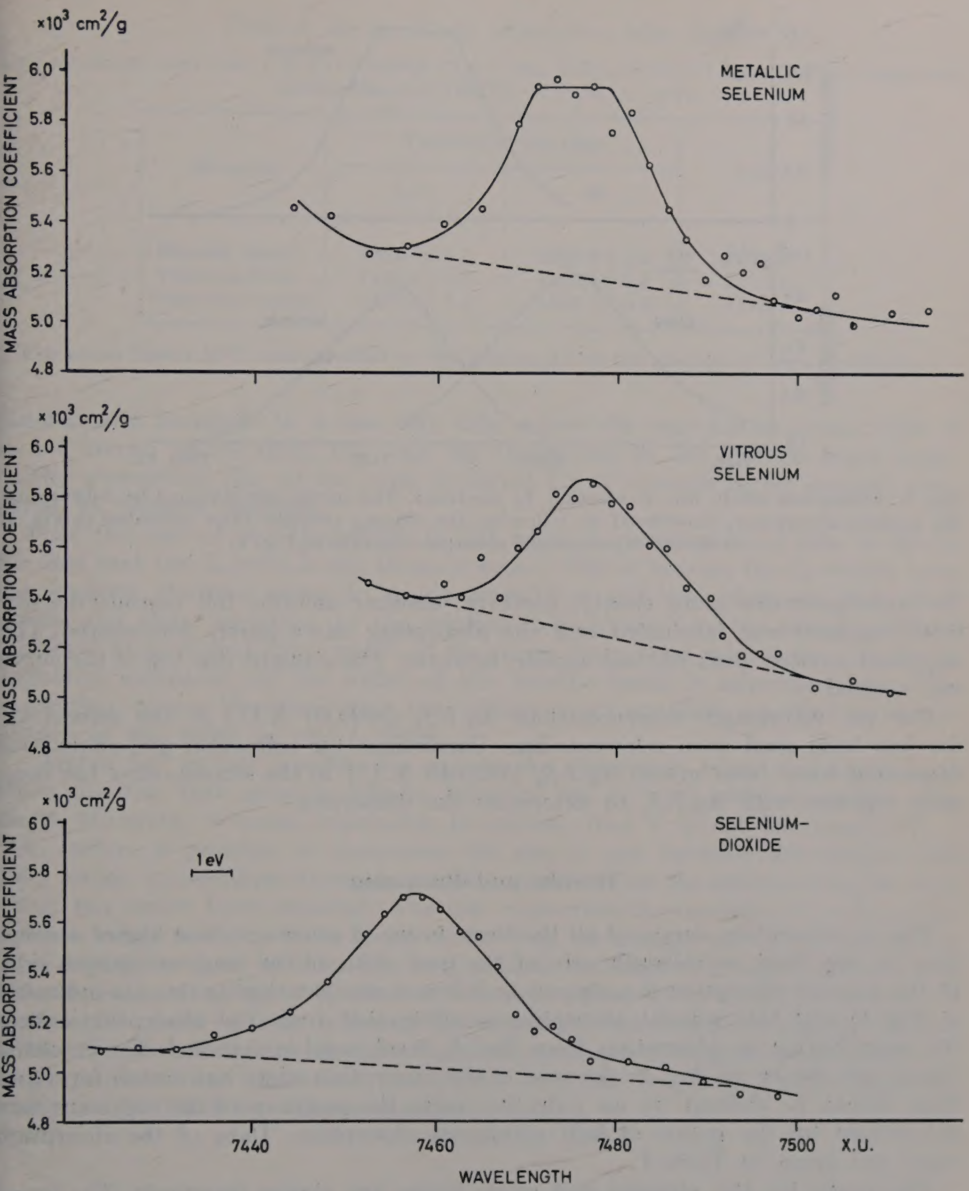

Fig. 1. The L_I X-ray absorption edges of metallic and vitreous selenium and of selenium dioxide.

separate determinations, each with a duration of 20 minutes. The total number of incident impulses per point is 40,000, which gives a statistical deviation in absorption coefficient of less than 1 %.

On the low frequency side of the edge in metallic selenium there is some evidence of a small peak which was suspected to originate from an exciton level.

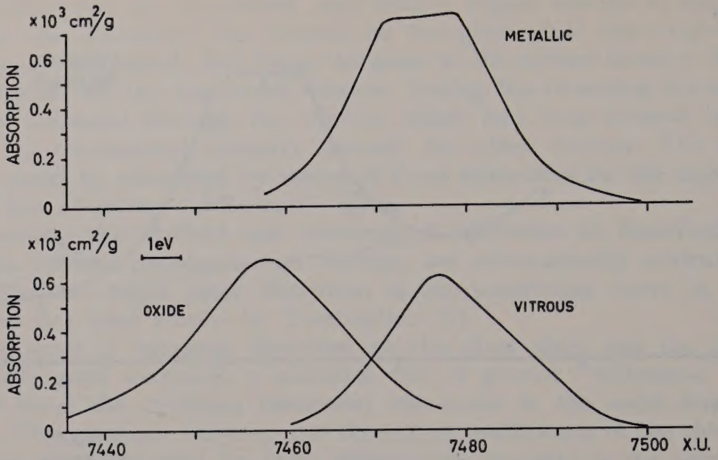

Fig. 2. Absorption solely due to ejection L_{I} electrons. The curves are obtained by subtracting the general absorption, considered as following the sloping straight lines indicated in Fig. 1, from the experimental absorption curves in Fig. 1.

To investigate this more closely, however, another metallic foil (surface density 0.368 mg/cm^2) was fabricated and the absorption curve partly remeasured. The supposed exciton peak did not appear, however. The straight line top of the curve was verified.

For the wavelength determinations Ag $L\beta_2$ (3695.60 X.U.) in the second order has been used as a reference line. Corrections for refraction and anomalous dispersion have been made. Ag $L\beta_3$ (3825.45 X.U.) in the second order has been used together with Ag $L\beta_2$ to determine the dispersion.

Results and discussion

The L_{I} absorption curves of all the three forms of selenium show higher absorption on the short wavelength side of the peak than on the long wavelength side. If the general absorption is supposed to follow a straight sloping line (as indicated in Fig. 1) and this general absorption is subtracted from the absorption curves the contribution in absorption from the L_{I} level itself is obtained. The resulting curves are shown in Fig. 2. As none of the absorption edges has arctan form and thus cannot be defined by an inflection point the positions of the edges are here determined by the points of half maximum absorption. Data of the absorption edges are given in Table 1.

The peaks for the vitreous and oxide forms are almost congruent. The upper part of the peak for the metallic form is broad compared to the other peaks. The absorption edge as well as the whole peak of the metallic selenium is shifted 0.5 eV towards shorter wavelengths compared to the edge and peak of vitreous selenium. It is not possible, however, to conclude anything concerning the positions of the lowest unfilled levels in the valence bands from this small shift. This is due to the facts that there is a difference in shape between the two edges, that the edges are not sharp and the definition of the wavelength positions is not

Table 1. Se L_I X-ray absorption edge data.

The constants used are: 1 X.U. = 1.00202×10^{-11} cm, 1 $Ry_\infty = 109737.3\ \mathrm{cm}^{-1}$. The energy conversion factor is 12372.2×10^3 (X.U.)·(eV).

Absorber	Position of the edge		ν/R
	X.U.	eV	
Metallic form	7484.7 ± 1.5	1653.0 ± 0.3	121.51
Vitreous form	7486.9 ± 1.5	1652.5 ± 0.3	121.47
Selenium oxide	7467.8 ± 1.5	1656.7 ± 0.3	121.78

The value 7490.4 X.U. was reported by Sandström (1) for the absorption edge of selenium.

theoretically founded. In a case like this, where the edge has no arctan form, it is not known where along the edge the transitions to the unfilled levels begin.

The absorption edge of the oxide is shifted 4.2 eV towards higher energies compared to vitreous selenium.

That the rise of the absorption at the edges is comparatively slow is due to the fact that the L_I level in the atoms is broad. This is because the L_I excited state has a short life-time owing to Auger transitions and intra-shell radiative transitions and thus, according to the relation $\Delta E \cdot \Delta t = h/2\pi$, the energy width of the level is increased. The width of the inner X-ray level, which may usually be neglected compared to the width of the valence band, is important here. The absorption curves therefore show the valence band structure modified by the influence of the width of the L_I level.

"Arctan fit" is not possible for any of the absorption edges and there is no other method that gives a definite value of the L_I level width from the edge shape. However, it seems reasonable to assume that it is not less than 2 eV.

In order, if possible, to determine the energy gap between the unfilled and filled bands in selenium experiments were made to find the emission line Se $L\gamma_{2,3}$ which has never been reported. The line represents the transition $L_I - N_{II,III}$ (L_I-valence band) and it is to be found on the long wavelength side of the absorption edge and quite close to this. The anti-cathode consisted of a copper plate coated with an evaporated layer of vitreous selenium about 10 μ thick. The line is too faint to be observed here, however. The explanation is that the vacancies created in the L_I subshell by the electron bombardment are to a great extent filled by Auger processes and intra-shell transitions, for which reason only a few vacancies remain to be filled by valence electrons.

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